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STANDARD METHOD FOR THE DISTILLATION OF GERANIOL

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Introduction

Commercial geraniol is the major constituent of the bait used in traps for the Japanese beetle (*Popillia japonica* Newman). The specifications^{1/} under which it is purchased include the statement, "not more than 5 percent boiling under 225° C. or more than 18 percent boiling over 245° (760 mm. pressure)."

Manufacturers of geraniol employ a diversity of methods and apparatus for the determination of the boiling range, and all of these differ from those used in the laboratory of this Division at Moorestown, N. J. As the results obtained are influenced markedly by the form of apparatus, rapidity of distillation, and barometric pressure, as well as other factors, it is desirable that a standard method be adopted. This paper is a study of some of these factors and describes the apparatus and methods now in use at this laboratory for the determination of the distillation range of geraniol to be used for Japanese beetle bait.

Various authorities^{2/}, ^{3/}, ^{4/} agree that an ordinary distilling flask is satisfactory for the determination of the boiling range. Gildemeister and Hoffman^{2/} and the Pharmacopoeia^{4/} state that the entire mercury column of the thermometer may be surrounded by the vapors of the distilling oil, but the former suggest that the thermometer be adjusted so that the top of

^{1/} Metzger, F. W., and Maines, W. W. Relation between the physical properties and chemical components of various grades of geraniol and their attractiveness to the Japanese beetle. U. S. Dept. Agr. Tech. Bul. 501, 14 pp., illus. 1935.

^{2/} Gildemeister, E., and Hoffman, F. The volatile oils. Second edition by E. Gildemeister, Vol. 1, 677 pp. 1919. London.

^{3/} Parry, E. J. The chemistry of essential oils and artificial perfumes. Ed. 3, Vol. 2, 344 pp. 1919. London.

^{4/} United States Pharmacopoeial Convention. Pharmacopoeia of the United States of America. Eleventh Revision. 1936.

the column of mercury is slightly above the outlet tube, while directs that the thermometer be adjusted so that the top of the column with the center of the opening of the outlet tube. The Pharmacopoeia also specifies that a condenser with a water jacket 40 to 60 cm. in length be used and that the distillation be conducted so that 4 to 5 ml. are distilled per minute.

The standard suggested in this circular takes into account (1) the length of the condenser, (2) the type of distillation flask, (3) the type of thermometer and the location of the bulb during distillation, (4) the rate of distillation, and (5) the effect of barometric pressure. An attempt was also made to use standard apparatus readily obtainable in the open market.

In comparing the results obtained on distillation of a commercial geraniol in the apparatus selected with those obtained in other distilling apparatus, it was found that: (1) The greater the length of the condenser, the higher is the observed boiling point. (2) The type of distilling flask (Engler or Ladenburg) was of little importance. (3) The closer the thermometer is to the level of the liquid, the higher is the observed boiling point. The Anschütz type thermometer, since it is completely within the neck of the distillation flask, eliminates the need for the application of a stem correction. (4) The observed boiling point varies directly with the rate of distillation. On this basis, the definite rate of distillation of not less than 3 or more than 4 ml. per minute is specified in the procedure. (5) A change in the barometric pressure of 20 mm. causes a change in the boiling point of 1° C. The effect of barometric pressure was determined from a series of distillations made at different pressures, several methods being used.

Apparatus

Flask.--Engler distilling, 100 ml. capacity, with the vapor tube 9 cm. above the surface of the liquid when the flask contains 100 ml., and with a neck 18.5 cm. in length. This flask conforms with the 1935 A. S. T. M. permanent standards, serial designation D 86 - 35, with the single exception that the neck of the flask is 18.5 cm. in length instead of 15 cm.

Condenser.--The condenser consists of a 9/16 inch \varnothing D seamless brass tube 22 inches long, located at an angle of 75° from vertical in a cooling bath of ice and water 15 inches long. This condenser conforms with the 1935 A. S. T. M. permanent standards, serial designation D 86 - 35.

Electric heater.--The electric heater is of such capacity (550 watts is sufficient) as to permit the first drop to fall from the condenser in not less than 8 or more than 10 minutes. It is fitted with a continuously adjustable rheostat and a refractory top 4-3/4 inches square with a 1-1/2 inch round hole.

Shield.--The shield is made of 22-gauge metal, asbestos lined. It fits snugly over and extends 11 inches above and 3/4 inch below the top of the heater. It is 4-3/4 inches square at the top end and 5-1/8 inches square at the bottom end. It is fitted with an asbestos-lined, tight-fitting cover

and a window, 7 inches long and 3 inches wide, of heat-resistant located 1 inch from the top and centered in the face. A slot tube, 6 inches long and 1/2 inch wide, extends upward from the bottom on a side adjacent to the window.

Thermometer.--The thermometer is of the Anschutz type with a National Bureau of Standards report. It has a range of from 200° to 270° C., subdivided in 1/2° intervals. It is approximately 130 mm. long and 6 mm. in diameter.

Receiving cylinder.--The receiving cylinder is a so-called normal or precision cylinder of 50 ml. capacity, having an internal diameter of 2 cm., and is graduated at intervals of 0.5 ml.

The assembled apparatus is shown in figures 1 and 2.

Procedure

(1) The condenser bath is filled with cracked ice, and enough water is added to cover the condenser tube. The temperature is maintained between 0° and 5° C.

(2) The condenser tube is swabbed to remove any liquid remaining from the previous test. A piece of soft cloth attached to a cord or copper wire is used for this purpose.

(3) Fifty ml. of the geraniol is transferred to the Engler flask by means of a pipette calibrated to deliver 50 ml. of geraniol at 25° C. The flask contains several small pieces of pumice or a few glass beads.

(4) The charged flask is placed in the 1-1/2 inch opening in the refractory top of the electric heater, and the vapor outlet tube is inserted in the condenser tube. A tight connection is made by means of a cork through which the vapor tube passes. The position of the flask is so adjusted that the vapor tube extends into the condenser tube not less than 1 inch or more than 2 inches. A soft plug of absorbent cotton is inserted about 1/2 inch into the neck of the distilling flask.

(5) The covered shield is placed so that it will be supported by the top of the heater.

(6) The receiving cylinder is placed at the outlet of the condenser tube in such a position that the condenser tube extends into the receiving cylinder at least 1 inch but not below the 50 ml. mark.

(7) When everything is in readiness, heat is applied at a uniform rate and so regulated that the first drop of condensate falls from the condenser in not less than 8 minutes or more than 10 minutes. As soon as the geraniol vapors start to rise in the neck of the distilling flask the cotton plug is withdrawn and the condensed water removed from the inside of the neck of the flask with filter paper. The thermometer provided with a cork is then fitted tightly into the flask so that it is in the middle of the neck

and so that the lower end of the capillary tube is on a level of the bottom of the vapor outlet tube at its junction with the flask, and the cover of the shield is replaced.

After the first drop falls from the end of the condenser the receiving cylinder is moved so that the end of the condenser tube touches the side of the cylinder. The heat is then so regulated that the distillation proceeds at a uniform rate of not less than 3 or more than 4 ml. per minute. The temperatures are observed when the volume of the distillate is 2.5 ml. (5 percent) and 41 ml. (82 percent). The distillation is stopped at this point to avoid the formation of a charred residue in the flask.

The observed temperatures are corrected to 760 mm. at 25° C. by subtracting 1° from the observed temperature for each 20 mm. above 760 mm. and adding 1° for each 20 mm. below 760 mm.

Accuracy of Results

With proper care and attention to detail, duplicate results obtained for the temperature at which 2.5 ml. (5 percent) is distilled should not differ from each other by more than 0.5°, while those for the temperature at which 41 ml. (82 percent) is distilled should not differ from each other by more than 1°.

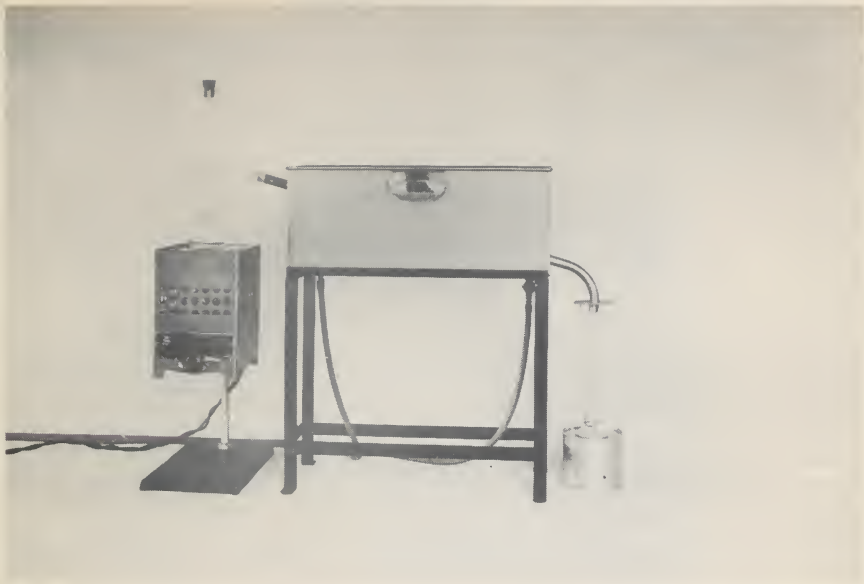


Figure 1.--Standard distillation apparatus without shield.

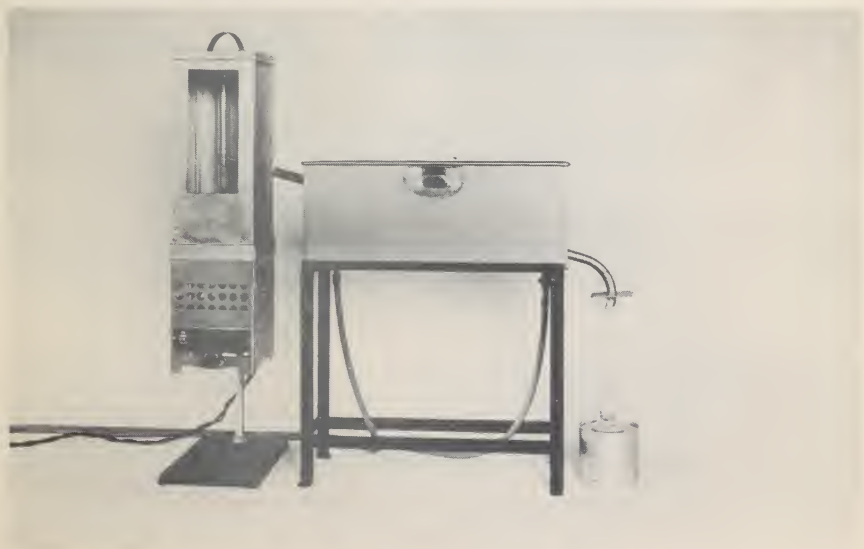


Figure 2.--Standard distillation apparatus, with shield in position.

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